

SULFATED METAL OXIDES AS CATALYSTS FOR COAL-OIL COPROCESSING

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ABSTRACT

We recently reported on the investigation of the catalytic activities of iron and tin oxides treated with varying amounts of sulfate for the direct liquefaction of Argonne coals.^{1,2} This paper deals with the use of the same catalysts in addition to novel bifunctional, bimetallic catalysts such as $\text{Mo/Fe}_2\text{O}_3\text{SO}_4^{2-}$ containing about 0.5 to 2 wt% of Mo on the sulfate-promoted oxide (20-100 ppm Mo with respect to coal) for coprocessing of Argonne Illinois No.6 coal with Maya (650°F) ATB oil (20% coal+80% oil). The properties of these sulfate-promoted iron oxides before reaction and the types of active phases formed under liquefaction conditions (determined by XRD, electron microscopy, and Mossbauer spectroscopy) are correlated with their apparent activities for coprocessing carried out at 400°C. The sulfated bifunctional catalysts containing about 3500 ppm Fe and 50 ppm Mo with respect to coal are highly active for coprocessing, giving 80+% total coal conversion and 70 % yield of lighter oils with Illinois No. 6 coal and Maya ATB. These conversion values are higher than those obtained with ferric sulfate or carbonyl precursors such as $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_6$. High catalyst dispersion and surface acidity are major factors that contribute to increased activity of these catalysts; Mo contributes a good hydrogenation function.

INTRODUCTION

The effects of catalytic activities of sulfate-treated iron and tin oxides and their relation to their catalytic activities in direct coal liquefaction have been reported.^{1,2,3} The high activity of these unsupported catalysts have been attributed mainly to their highly dispersed forms (available surface area per gm of catalyst) and to their enhanced surface acidity.

It is important to note that these sulfated oxides [$\text{M}_x\text{O}_y/\text{SO}_4^{2-}$] do not have real stoichiometric formulas but are a symbol for oxides which contain chemically attached surface species usually constituting a few percent of the total oxide. With $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, for instance, this could be considered as SO_3 chemisorbed on the Fe_2O_3 surface. We have found⁴ that the presence of a very small amount of moisture in the catalyst system helps maintain high acidic activity, likely due to transformation of the catalyst to its Bronsted acid form, responsible for generating carbocations.

The effects of various anions such as Cl^- , PO_4^{3-} , and SO_4^{2-} in the form of dopants added to metal oxides to decrease their particle size has been the topic of considerable interest in material science since the early eighties. It is known⁵ that the sulfate anion prevents sintering of ceramic oxide powders during calcination, thereby reducing the degree of crystallinity and

lowering the average crystallite size of these oxides. It has been shown that¹ the superacid $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ forms a highly dispersed catalyst in the form of particles of about 30-100 Å units in diameter. It is this very property that also makes sulfated iron oxides good sensors for combustible gases.⁵

Addition of molybdenum to the sulfated iron oxide provides an excellent hydrogenation function to contribute to the catalytic action of the highly dispersed, superacidic $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$.

EXPERIMENTAL

Catalyst Preparation and Characterization: The $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalysts consisting of varying amounts of molybdenum were prepared using homogeneous coprecipitation followed by an incipient wetness technique. Ammonium heptamolybdate was used as a starting salt for molybdenum impregnation. Conditions for the preparation of these catalysts are given in Table 1. The catalysts were characterized by BET-surface area analysis, sulfur analysis, thermal stability measurements, X-ray diffraction, and electron microscopy. A Phillips X-ray Diffractometer using Cu-K α radiation at 30 kV and 25 mA was used to obtain the powder diffraction patterns of the catalysts.

Average crystallite sizes of these catalysts were calculated from line broadening of the peaks, corrected for instrumental broadening. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were carried out for structural investigation of the catalysts using JEOL 35 CX SEM and JEOL 200 CX TEM models. The residues of coal liquefaction experiments were also analyzed using X-ray diffraction and a JEOL 2000 FX STEM (100 kV beam) with an energy dispersive X-ray spectrometer (EDX) to determine composition and dispersion information about the catalytic phases formed under liquefaction conditions.

Reaction Studies: Coprocessing experiments were conducted in a 300ml stainless steel autoclave (Autoclave Engineers) agitated by a turbine impeller and heated by a tube furnace. Coal (10.0g), 40.0g Maya ATB residuum, and the desired catalyst precursors/sulfated catalysts were placed into the reactor, which was flushed with helium and stirred at 50°C for two hours to ensure mixing of the catalyst precursor in the viscous residuum. The reactor was pressurized with hydrogen to 6.9 MPa, heated to reaction temperature (400 or 425°C) in 30 minutes, and held there for 60 minutes while stirring at 1400 rpm. The reactor was then cooled to below 300°C in about five minutes. Soxhlet extraction with methylene chloride was used to determine conversion. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles were determined by adding 40 volumes of n-pentane to the methylene chloride (CH_2Cl_2) solubles and then using Soxhlet extraction with n-pentane. Transmission electron microscopy was carried out using a JEOL 2000FX STEM (100kV beam) with an energy dispersive X-ray spectrometer.

RESULTS AND DISCUSSION

Catalyst Characterization: The iron and tin oxides treated with different amounts of sulfate were characterized by DTATGA to determine their thermal stability. For sulfated iron oxides promoted with small amounts of molybdenum, $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, decomposition of the sulfate group was found to occur above 600°C under an N_2 atmosphere. The effects of sulfate anion on reduction of grain sizes were published earlier.³ The average crystallite size

of the oxide particles had decreased upon treatment with 2 to 6 wt % of sulfate anion; this was accompanied by a corresponding increase in the specific surface area of these oxides, observed when liquid nitrogen physisorption was carried out using the BET method. A linear relationship was observed between the concentration of sulfuric acid used for sulfate treatment and the final amounts of SO_4^{2-} groups on the iron oxides up to about 8 wt% sulfate loading. From X-ray diffraction studies of the sulfated iron oxides, α - and γ - Fe_2O_3 were found to be the most abundant crystalline phases, while for tin oxides, the most abundant phase was crystalline SnO_2 . Catalyst characterization results are listed in Table 2. For $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ containing 20-100 ppm of Mo with respect to coal, no molybdenum was detected by X-ray diffraction; this could be due to the very fine dispersion of Mo apart from its small concentration on the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst. Temperatures of the onset of liquefaction of Illinois No.6 coal using different sulfate-treated oxides as catalysts are listed in Table 2. These temperatures were determined using a high pressure, high temperature polarizing optical microscope with flowing H_2 at 300 psig pressure. $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalysts were also characterized by electron microscopy and found to have a grain size of about 10-15 nm. The amounts of Mo in the catalysts were determined by inductively coupled plasma analysis.

Reaction Studies: Initially a thermal (no added catalyst) run was carried out to determine the catalytic activities of the mineral matter (especially pyrite) inherent in coal. The coal conversion values listed in this paper are calculated based on weight of the final residue.

(I) Activities of the Sulfated Oxides

The sulfated iron and tin oxides were used in small concentrations for coprocessing of Illinois No. 6 with Maya ATB. Use of the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst containing about 3.4 wt% of sulfate group, resulted in a coal conversion of 70 wt % with 72 wt % selectivity to oils at 400°C with about 3500 ppm iron with respect to the coal-oil mixture. When $\text{SnO}_2/\text{SO}_4^{2-}$ (3.9 wt% sulfate) was used as the catalyst with 3500 ppm of tin at 400°C, about 62 wt% conversion was obtained with about 76 wt% selectivity to oils. A reaction was carried out with a molybdenum containing catalyst precursor, $\text{Mo}(\text{CO})_6$, for comparison, using about 100 ppm Mo with respect to the mixture of coal and oil. This resulted in a 71 wt% coal conversion with 70 wt% selectivity to lighter oils. Use of a bimetallic, bifunctional catalyst, $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$, consisting of 50 ppm Mo and 3500 ppm Fe with respect to the coal-oil mixture gave a coal conversion of 80 wt% with 80 wt% selectivity to lighter oils. The higher activity of this catalyst is attributed to the hydrogenation ability of Mo and, possibly, to the acid sites of the sulfated catalyst. Results of these catalyst activity comparisons and those obtained in the coprocessing reaction employing a bimetallic sulfated oxide of iron and tin, $\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, (with 1750 ppm of each iron and tin) are shown in Figure 1(A).

Enhancement in total conversions as well as conversions to oils obtained with sulfated oxides are attributed mainly to enhanced "dispersions" (surface area/gm) with a possible contribution from the high surface acidity of these oxides upon sulfate treatment. It is likely that, with increase in the specific surface area and decrease in the average particle size of the oxides upon addition of small amounts of the sulfate group, conversion of the oxides to active catalytic sulfide phases, especially non-stoichiometric sulfides of iron, is facilitated.⁶ More of the active catalyst surface of these sulfides becomes available for reaction.

(II) Activity of $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ Catalysts at 400 and 425°C

Addition of small amounts of Mo to 0.5 to 2 wt% of the sulfated iron oxides (about 20-100 ppm Mo concentration with respect to the coal-oil mixture) resulted in substantial improvement in the selectivity to oils. A series of experiments were carried out to determine the coprocessing conversion of Illinois No. 6 with Maya ATB at two different reaction temperatures (400 and 425°C) and for different amounts of Mo loadings on $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. The results of experiments carried out at 400 and 425°C are shown in Figure 1(B).

Total coal conversions, as well as selectivities to lighter oils, increased for both temperatures with the amount of molybdenum in the sulfated iron oxide catalyst (0-100 ppm Mo with respect to the coal-oil mixture). Conversions as high as 84 wt% (maf coal) with selectivity values of higher than 80 wt% were obtained at about 100 ppm Mo + 3500 ppm Fe added in the form of $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$. Surprisingly, we obtained slightly lower values for both coal conversion and selectivity to oils in almost all the reactions carried out at 425°C as compared to those at 400°C. This apparent decrease in coprocessing conversion is likely due to the extensive coking reactions occurring because of the presence of an acidic functionality in the catalyst. The coal liquefaction residues obtained in this case (425°C) had a rock-like appearance.

All of the aforementioned reactions were carried out without adding any external sulfur compound since Illinois No. 6 coal and the heavy oil (Maya ATB) together have enough sulfur to sulfide the added metals during reaction. Nevertheless, a run was made with addition of elemental sulfur (10% in excess of that required for complete sulfidation of both the Fe and Mo in the catalyst) to the coal-oil mixture prior to reaction at 400°C with 3500 ppm of iron and 100 ppm of Mo. No effect of the added sulfur was observed on either overall coal conversion (86 wt%) or the selectivity to lighter oils (82 wt%).

Product Characterization:

(I) Elemental Analyses of Methylene Chloride-Soluble Products

The methylene chloride solubles of the coprocessing product from using the Fe-Mo precursor were analyzed for C,H,N, and S contents. As seen from Table 3, an improvement in the H/C atomic ratios is obtained for the soluble products for the sulfated iron oxides containing small amounts of molybdenum as catalysts. At the same time, a significant degree of sulfur and nitrogen removal (75 to 80 % HDN and HDS) is obtained. With the $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalysts, this could be attributed to the enhanced acidic strength and high dispersions of the catalysts and the hydrogenative function contributed by Mo.

(II) X-Ray Diffraction and Electron Microscopy of Residues

X-ray diffraction (XRD) was performed on the methylene chloride-insoluble fraction of the coprocessing runs carried out with Illinois #6 coal with added iron catalysts. Transmission electron microscopy was employed to determine the size range of the iron- and molybdenum-containing particles produced from $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_6$ precursors. To eliminate interference of the iron and other mineral matter in the coal, a model system was used which consisted of activated carbon with molybdenum or Fe-Mo deposited on it. This mixture was produced by heating a mixture of activated carbon (with a very low iron content), toluene (solvent), and $\text{Mo}(\text{CO})_6$ with or without $\text{Fe}(\text{CO})_5$ in an autoclave to decompose the precursor into small particles, some of which would end up on the carbon support. Similarly, for the electron microscopic studies, a $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst was deposited on an activated carbon matrix using tetralin as dispersion medium. These TEM images show the catalyst particles containing Fe and Mo on active carbon with sizes ranging from 10-30 nm.

CONCLUSIONS

Sulfated iron and tin oxide catalysts were found to be active for the coprocessing of Argonne Illinois No.6 coal with Maya ATB (20:80 coal:oil) both at 400 and 425°C. For a bimetallic catalyst, $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$, consisting of 50 ppm Mo and 3500 ppm iron, a 78 % coal conversion of Illinois No. 6 was obtained with an oil- selectivity of 80 % at 400°C. The sulfated iron oxide catalysts with small amounts of Mo(20-100 ppm) were more active than the soluble precursors of the same metals at 400°C. Significant HDN (~75 %) and HDS(~80%) were obtained with Mo-promoted sulfated iron oxide catalysts. We attribute the higher activity of the sulfated oxides to their fine grain size (30-100 Å) with increased catalyst dispersion and to increase in their acid strength. The comparison between the activities of sulfated oxides and the soluble precursors shows that finely divided solid catalysts could be as active as the catalysts produced from the soluble precursors of iron and molybdenum. Thus, the catalytic activity of the sulfated oxides are the result of several factors: the fine grain size is probably of the greatest importance, the superacidity of the starting catalysts may play a part during the initial phases of the reaction. In the case of $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$, the hydrogenation ability of Mo certainly plays a part. However, there is still much to be learned about the mechanisms involved in these types of reactions. With these superacidic sulfated metal oxides as catalysts, the chemistry of the reactions in coal liquefaction could be different from what is known so far (such as possible involvement of radical ion intermediates). These finely divided solid catalyst-precursors therefore show great promise for application in hydroprocessing reactions

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of the Argonne coal sample bank for providing the coal samples, C. van Ormer and J.R. Blachere for the transmission electron microscopy, the donation of Maya crude by CITGO, and funding support from the U.S. Department of Energy under grant number DE-FC22-88PC8806.

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Table 1. Preparation Conditions of Sulfated Iron and Tin Oxides

Catalyst	Catalyst Designation	Starting Salts	Norm. H ₂ SO ₄	Calcination, T°C
Fe ₂ O ₃ /SO ₄ ²⁻	I	Fe Alum ^a	--	500
Mo/Fe ₂ O ₃ /SO ₄ ²⁻	II	Fe Alum ^a	--	500
Mo/Fe ₂ O ₃ /SO ₄ ²⁻	III	Fe Alum ^a	--	500
Mo/Fe ₂ O ₃ /SO ₄ ²⁻	IV	Fe Alum ^a	--	500
SnO ₂ /SO ₄ ²⁻	V	SnCl ₄ /5H ₂ O	6.0	600
SnO ₂ /Fe ₂ O ₃ /SO ₄ ²⁻	VI	Chloride Salts ^b	6.0	500

^a Urea was used as the precipitating agent whereas ammonium heptamolybdate was used to impregnate small amounts of Mo on sulfated iron oxide before calcination.

^b The ferric and tin chloride salts were used here with 28 % ammonia water as a precipitation agent.

Table 2. Physicochemical Properties of the Sulfated Oxide Catalysts

Catalyst	Wt % Mo	S _g , m ² /g	XRD: D _{avg}	TEM :D _{avg}	Onset T°C ^a
Catalyst I	0.0	81.72	16 nm	20-25 nm	410
Catalyst II	0.4	81.50	12 nm	20-30 nm	nd
Catalyst III	1.0	88.00	9 nm	15-20 nm	400
Catalyst IV	2.0	92.21	9 nm	10-15 nm	400
Catalyst V	--	146.23	5 nm	10-15 nm	385
Catalyst VI ^b	--	320.00	5 nm	5-10 nm	nd

^a Onset coal liquefaction temperature for a non-catalytic liquefaction run for Argonne Illinois No.6 coal was 450°C as determined using a high temperature, high pressure polarizing microscope.

^b This catalyst consisted of equal weight percents of SnO₂ and Fe₂O₃.

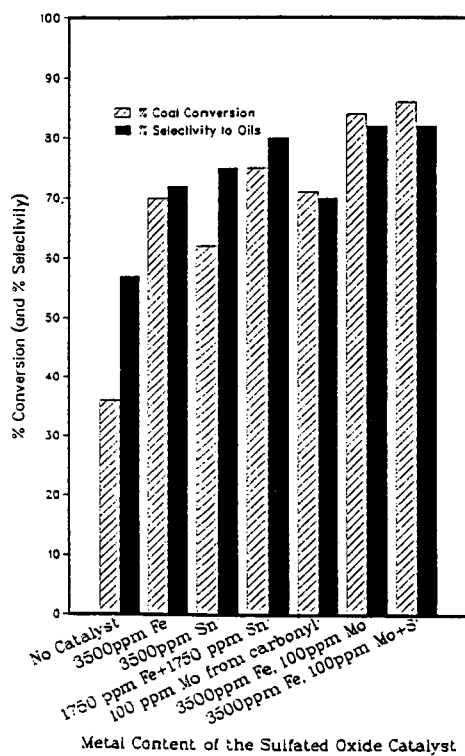
Table 3. Elemental Analysis of CH₂Cl₂ Solubles Obtained from Coprocessing of Illinois No.6 and Maya with Different Catalysts

Amount of Catalysts vs. Analysis : Wt %							
Catalyst	ppm Mo	ppm Fe	% C	% H	% N	% S	{H/C}atom
None	--	--	83.00	10.30	0.25	3.18	1.49
Catalyst III	50	3500	47.58	5.83	0.55	2.01	1.47
Catalyst IV	100	3500	66.99	8.52	0.72	2.13	1.53
Fe(CO) ₅	--	5000	83.83	10.45	0.33	3.01	1.50
Carbonyls	500	5000	82.53	10.79	0.43	2.94	1.57
Mo-naph. ^b	500	5000	83.07	10.50	0.40	2.89	1.52

^a All runs were made with Illinois No.6, 425°C, 1000 psig cold H₂, 60 minutes, 20 wt% coal/80 wt% Maya ATB.

^b Fe(CO)₅ was used in this run with Mo-naphthenate.

A



B

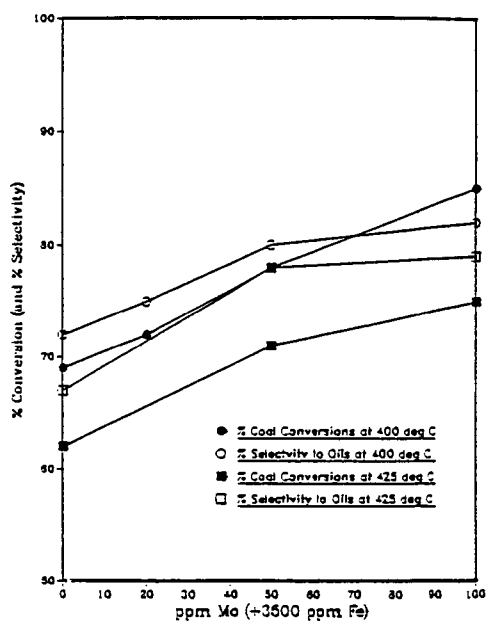


Figure 1. (A) Activity of Sulfated Metal Oxides for Coprocessing of Illinois No.6 Coal at 400°C, 1000 psig cold H₂, 1h and (B) Activity of Mo/Fe₂O₃/SO₄²⁻ Catalysts for Coprocessing at 400 and 425°C, 1000 psig cold H₂, 1h